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Long-range order and lattice mismatch in metallic superlattices

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A general diffraction relation for crystalline-crystalline superlattices, including random interfacial disorder of a Gaussian type induced by the lattice mismatch between the constituents, is derived and applied to superlattices composed of materials with large symmetry and lattice-parameter difference. The interfacial disorder caused by an important lattice mismatch is found to be responsible for the reduced long-range order at large scattering vector observed in many superlattices. Moreover, the increase of the interfacial disorder with lattice mismatch and modulation wavelength shows the importance of misfit dislocations in addition to interfacial roughness.

X-ray diffraction has been commonly used to characterize the chemical and structural modulation in superlattices.[1] However, as all phase information is lost in diffraction experiments, experimental data cannot be converted directly into structural information. Theoretical models must be developed and fitted to the data.

A variety of models for compositionally modulated structures have been derived. The "step" model assumes an abrupt composition profile with bulk lattice spacings for each material. The "strain" model assumes lattice-spacing variations due to in-plane coherency strains. These one-dimensional models have been successfully used in semiconducting and metallic superlattices to derive peak positions and relative intensities.[2-5] In most superlattices however, the linewidth of the high-angle reflections is much larger than predicted by these models. The structural coherence length (ξ) derived from the full width at half maximum of these peaks using Scherrer's equation rarely exceeds a few times the modulation wavelength (Λ). A mechanism reducing the long-range order needs to be included in the models.

In more realistic models, Gaussian type continuous or discrete fluctuations of the individual layer thickness,[6,7] the modulation wavelength,[8,9] the number of atoms in a layer,[10,11] and the lateral thickness[12] are taken into account. At high angle (large q), a discrete distribution of width c^{-1} equal to an interplanar distance gives rise to a slight reduction in diffraction peak intensity and a disappearance of the secondary peaks.[10,11] On the other hand, a continuous distribution of the amorphous layer thickness, of width $c^{-1} \simeq 2$ Å, on the thickness of the amorphous layer, explains the total loss of high-angle superlattice peaks in crystalline-amorphous systems.[6]

Fluctuations are caused by different mechanisms such as imperfections in deposition process or geometric constraints at the interfaces due to the differences in lattice parameter and symmetry. The geometric constraints can be accommodated by distorting the layers or the interfaces. This can be achieved by the introduction of an in-plane coherency strain, or by the creation of misfit dislocations. The former mechanism occurs in multilayers with a small ($\leq 1\%$) lattice mismatch [Nb/Al (Ref. 13), Nb/Ta (Ref. 14)] while the latter mechanism is present in multilayers with an important lattice mismatch [Nb/Cu (Refs. 4 and 15), Pb/Ag (Refs. 16 and 17), Fe/Mg (Ref. 9), Mo/Ni (Ref. 18), Pd/Au (Ref. 8), and Fe/V (Ref. 19)]. A transition from a coherent to an incoherent structure is observed in multilayers with a small lattice mismatch as the modulation wavelength increases.[13]

In this paper, we derive a kinematical diffraction relation for crystalline-crystalline superlattices including disorder *concentrated only at the interface.* This relation is applied to superlattices with large differences both in lattice parameter and symmetry. All the studied systems form superlattices with sharp interfaces, as their constituents do not form solid solutions in their thermodynamic phase diagram. Coherency strains, if present, are small in these systems, justifying the use of the bulk lattice parameters.

We assume that the distance at the interface between unlike atoms fluctuates around an average value $\bar{a}$ following a continuous, Gaussian distribution of width c^{-1}. The origin of this fluctuation can be the perpendicular lattice mismatch $\delta = (d_a - d_b)/\max(d_a, d_b)$, with d_a and d_b the lattice spacings of the constituents, which is correlated with the in-plane lattice parameter difference. The geometric conditions imposed by the latter create a "rough" interface, with large (atoms A forced on top of atoms B) and small (atoms A "falling" in between atoms B) interface distances, assumed to follow a Gaussian distribution around an average value $\bar{a}$. This assumption is strictly correct for incommensurate systems and only approximately correct for systems that have a long-distance commensurate relationship. The total intensity is given as the integral of the square of the structure factor $F(q)F(q)^*$ (Refs. 20 and 21):

$$I(q)=M[A^2+B^2+2AB\exp(-q^2/4c^2)\cos(q\Lambda/2)]$$
$$+2\sum_{m=1}^{M-1}(M-m)\{(A^2+B^2)\exp(-2mq^2/4c^2)\cos(2mq\Lambda/2)+AB\exp[-(2m+1)q^2/4c^2]\cos[(2m+1)q\Lambda/2]$$
$$+AB\exp[-(2m-1)q^2/4c^2]\cos[(2m-1)q\Lambda/2)]\}, \quad (1)$$

with

$$A=f_a\frac{\sin(N_aqd_a/2)}{\sin(qd_a/2)}, \quad (2)$$

$$B=f_b\frac{\sin(N_bqd_b/2)}{\sin(qd_b/2)}, \quad (3)$$

$$\Lambda=(N_a-1)d_a+(N_b-1)d_b+2\bar{a}, \quad (4)$$

with M the number of crystalline blocks of materials A and B with f_a and f_b the scattering powers, and N_a and N_b the number of planes, respectively.

For $c^{-1}=0$, Eq. (1) reduces to the step model, while for $c^{-1}=\infty$ it reduces to the scattering of two independent blocks of materials A and B without any trace of superstructure. For crystalline-amorphous multilayers, Eq. (5) of Ref. 6 recovered when $f_b=0$.

Using Eq. (1), the high-angle x-ray-diffraction pattern of a Nb/Cu multilayer is calculated for different values of the distribution width c^{-1}, normalized to the interface distance $\bar{a}$, conventionally taken to be $(d_a+d_b)/2$ (see Fig. 1). In this calculation, all correction factors (polarization factor, Lorentz factor, Debye-Waller factor, atomic density of the planes, atomic structure factor) are included. A drastic decrease of the peak intensities together with an important increase of the linewidths is observed with increasing c^{-1}.

For a perfect superlattice the long-range order extends through the whole sample. Interfacial disorder can strongly reduce this order and can be obtained by extracting ξ from the linewidth of theoretically calculated spectra, using Eq. (1), as a function of the fluctuation amplitude (distribution width c^{-1}). For $c^{-1}=0$, ξ/Λ equals the number of bilayers composing the superlattice, while for $c^{-1}=\infty$, the normalized coherence length becomes 0.5 (i.e., the coherence length due to a single crystalline layer) since we assumed equal thickness layers. Superlattice structure will be observed in the diffraction pattern as long as $\xi/\Lambda \geq 1$, which corresponds to a fluctuation amplitude of $\simeq 40\%$. We simulated the evolution of x-ray spectra versus the interfacial disorder for five different systems (Nb/Cu, Mo/Ni, Pd/Au, Pb/Ag, and Fe/V), and found that the loss of coherence versus interfacial disorder is *universal*, as expected.

The x-ray spectra of five systems with different lattice mismatch δ and symmetry were analyzed to study the interfacial disorder as a function of Λ. Results for systems with identical symmetry (bcc-bcc or fcc-fcc) are presented separately [Fig. 2(a)], from systems with different symmetry (bcc-fcc) [Fig. 2(b)].

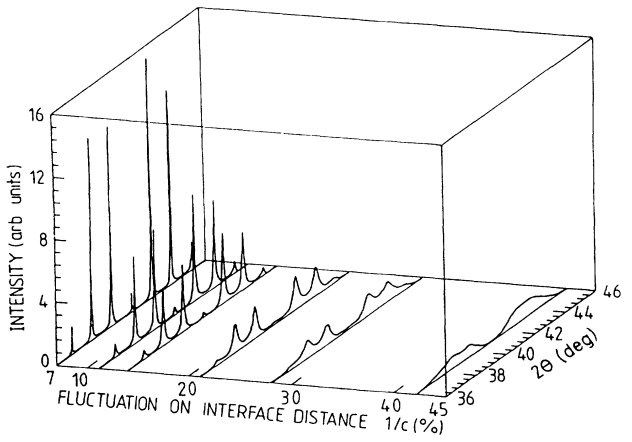

FIG. 1. Evolution of simulated high-angle Nb/Cu spectra for different values of c^{-1}, for $d_a=2.33$ Å, $d_b=2.08$ Å, $N_a=N_b=24$, $\bar{a}=(d_a+d_b)/2$.

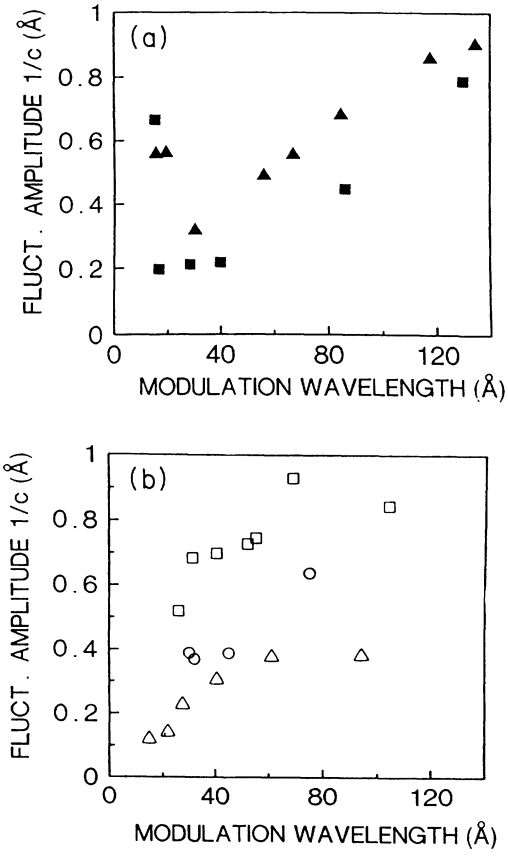

FIG. 2. Fluctuation amplitude c^{-1} in absolute units vs modulation wavelength for (a) Nb/Cu (▲), Mo/Ni (■) multilayers and (b) Pd/Au (△), Fe/V (○), and Pb/Ag (□) multilayers. Note that in (a) the smallest nominal modulation wavelength samples are amorphous or strongly disordered as indicated by their x-ray linewidth.

For small Λ (neglecting the very small Λ region where the layers become amorphous), the value of the interfacial disorder is very close to the difference in lattice parameter. In Nb/Cu for instance, the difference in lattice parameter is equal to 0.25 Å (2.33–2.08 Å), while the fluctuation amplitude for a superlattice with $\Lambda = 30$ Å is near 0.3 Å. The agreement between these two values suggests that this type of interfacial disorder, induced by the lattice mismatch, possibly is responsible for the observed linewidth in superlattices with small modulation wavelength. The derived fluctuation amplitude from the spectrum with the *smallest* experimental Λ versus the difference in lattice parameter is plotted in Fig. 3. The observed linear dependence strongly supports our interpretation, although more experimental data at small Λ are necessary. It is quite interesting that with the exception of Fe/V, the fluctuation amplitude varies systematically with lattice mismatch, in a number of systems, prepared in different laboratories. Clearly, the existence of such a dependence is indicative of the fact that the underlying physical mechanism has been properly identified. Moreover, the fact that this dependence extrapolates through the origin lends strength to this model since in a perfectly matched system (i.e., lattice mismatch $=0$) no fluctuations are expected ($c^{-1}=0$).

Surprisingly, the interfacial disorder is not constant as a function of the modulation wavelength which cannot easily be understood from purely geometrical arguments. In order to explain these features, an additional disordering mechanism (different from the geometrical arguments), depending on the lattice mismatch and the modulation wavelength, must be invoked.

Hilliard[22] calculated the evolution of dislocation and coherency strain energy versus Λ for superlattices with a fixed δ. The dislocation energy, needed to introduce a dislocation at the interface, is inversely proportional to Λ and δ, whereas the coherency strain energy needed to impose an overall change of in-plane lattice spacing is proportional to Λ and δ. Therefore, strains are energetically favorable at low Λ, while dislocations become increasingly favorable at high Λ and δ. Within the framework of the present paper, the distribution width c^{-1} could be interpreted as the combination of two types of disorder. The first type is strictly related to the geometrical considerations imposed by the difference in lattice parameter, while the second type is a measure for the dislocation density

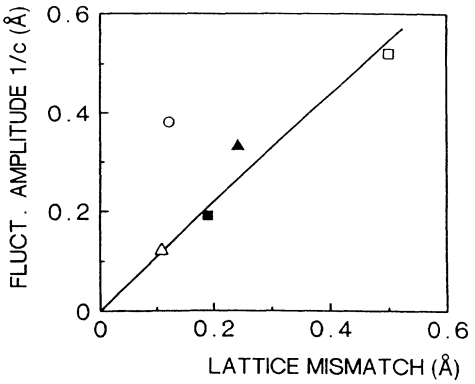

FIG. 3. Fluctuation amplitude c^{-1} in absolute units vs the lattice mismatch in absolute units, for the smallest experimental Λ in the five systems. The line is a guide to the eye.

near the interface.[8] The combination of both explains qualitatively the observed increase of interfacial disorder as a function of Λ and δ, and indicates the presence of dislocations for large lattice mismatch.

In summary, we derived a new diffraction relation for crystalline-crystalline superlattices which includes interfacial disorder. We found that the lattice mismatch can provide the amount of disorder necessary to explain the reduced long-range order observed in high-angle diffraction peaks in superlattices with large differences both in lattice spacing and symmetry. Furthermore, it was shown that the interfacial disorder extracted from experimental data is strongly dependent on the lattice mismatch and the modulation wavelength, which indicates the presence of interfacial dislocations.

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